

**ELECTRIC DOUBLE LAYER CAPACITOR, ELECTRODE BODY, AND MANUFACTURING METHOD**

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**Inventor:** KAWASATO TAKESHI; HIRATSUKA KAZUYA; IKEDA KATSU HARU; YOSHIDA NAOKI  
**Applicant:** ASAHI GLASS CO LTD  
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**Abstract of JP2001307966**

**PROBLEM TO BE SOLVED:** To provide an electric double layer capacitor with superior long reliability in operation and a small deterioration of performance in charge/discharge cycle.

**SOLUTION:** The electric capacitor with organic electrolytic solution has an electrode body. In the electrode body, a carbon-based sheet-like electrode made mainly of activated carbon is joined to a charge collector through a carbon-based conductive layer containing polycarbodiimide resin as a binder element.

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(71) 出願人 000000044

旭硝子株式会社

東京都千代田区有楽町一丁目12番1号

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平成12年4月27日 (2000.4.27)

(72) 発明者 河里 健

神奈川県横浜市神奈川区羽沢町1150番地

旭硝子株式会社内

(72) 発明者 平塚 和也

神奈川県横浜市神奈川区羽沢町1150番地

旭硝子株式会社内

(72) 発明者 池田 克治

神奈川県横浜市神奈川区羽沢町1150番地

旭硝子株式会社内

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(54) 【発明の名称】 電気二重層キャパシタ、そのための電極体及びその製造方法

(57) 【要約】

【課題】 充放電サイクルによる性能劣化が少なく、長期の作動信頼性に優れた電気二重層キャパシタを提供する。

【解決手段】 有機電解液を有する電気二重層キャパシタにおいて、活性炭等を主体としシート状に成形された炭素質電極が、ポリカルボジイミド樹脂をバインダ成分として含む炭素系導電性層を介して集電体と接合された電極体を使用する。

ジイミド樹脂をバインダ成分として含む炭素系導電性層を介して集電体に接合されていることを特徴とする電気二重層キャパシタ及びそのための電極体を提供する。

【0009】また、本発明は、炭素質粉末と結合材とを含む混合物をシート状に成形して炭素質電極を形成し、該炭素質電極を、ポリカルボジイミド樹脂をバインダ成分として含む炭素系導電性接着層を介して集電体に接合し、150℃以上で加熱することを特徴とする電気二重層キャパシタ用電極体の製造方法を提供する。

【0010】

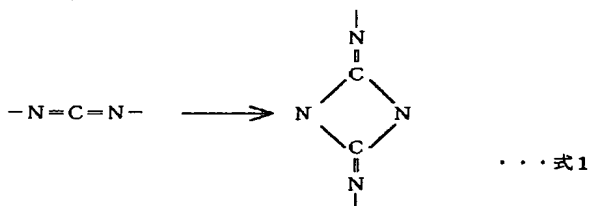
【発明の実施の形態】本明細書において、炭素質粉末と結合材とを含む炭素質電極を集電体と一体化させたものを電極体という。そして、この電極体を正極側に用いる場合は正極体、負極側に用いる場合は負極体という。

【0011】本発明の電気二重層キャパシタにおいて、炭素質電極に含まれる結合材はポリカルボジイミド樹脂であり、この樹脂の耐熱温度は通常200～400℃の範囲であり耐熱性が高い。ポリカルボジイミド樹脂は、その主鎖にカルボジイミド基(—N=C=N—)の骨格を有するものの総称であって、耐薬品性、機械的性質、寸法安定性、電気的特性において優れている。

【0012】ポリカルボジイミド樹脂は、加熱により溶融し、内部架橋反応が起こって硬化する。さらにポリカルボジイミド樹脂に、分子中に2個以上の反応基を有する架橋剤を混合して加熱すると、ポリカルボジイミド樹脂は効果的に加熱硬化する。ポリカルボジイミド樹脂の内部架橋反応は、例えば式1で示される反応である。

【0013】

【化1】



【0014】本発明において使用されるポリカルボジイミド樹脂としては、具体的には例えばR<sup>1</sup>—(—N=C=N—R<sup>2</sup>—N=C=N—)<sub>m</sub>—R<sup>3</sup>で表されるポリカルボジイミド樹脂が好ましく使用できる。ただし、式中R<sup>1</sup>及びR<sup>3</sup>はそれぞれ独立に1価の有機基であり、R<sup>2</sup>は2価の有機基であり、mは正の整数である。上記のようなポリカルボジイミド樹脂は、例えばOCN—R<sup>2</sup>—NCOとR<sup>1</sup>—NCOとR<sup>3</sup>—NCOを原料として反応させて得ることが好ましい。

【0015】ポリカルボジイミド樹脂は、市販品では粉末状の樹脂、樹脂を溶剤に溶解した溶液(ワニス)、溶剤を含まないペースト状の樹脂及びフィルム状に成形された樹脂があるが、ペースト及びワニスは塗工液を作製しやすいので好ましい。市販されているポリカルボジイミド樹脂のワニスには、例えば日清紡社の「カルボジラ

イト」がある。

【0016】本発明の電気二重層キャパシタ用電極体においては、炭素系導電性層のバインダ成分であるポリカルボジイミド樹脂の耐熱性が高いため、高温下での加熱処理又は減圧下の加熱処理によって電極中に含まれる水分を高度に乾燥除去できる。また、ポリカルボジイミド樹脂は有機電解液に対する耐性があり、さらに電極シートの結合材として含フッ素樹脂が含まれていても電極シートと金属等の集電体との接着強度をきわめて高いものとする。このため、大電流密度で充放電サイクルを繰り返しても、長期間にわたって電圧を印加しても、電気二重層キャパシタは作動性能が安定しており、電極の内部抵抗の増加を小さくできる。

【0017】バインダ成分に用いる樹脂は、樹脂粉末として使用することもできるし、ペースト状のものをそのまま使用することもできるし、樹脂粉末、樹脂を含むワニス又はペースト状の樹脂を溶媒に分散させてスラリーとして使用することもでき、フィルム状に成形して使用することもできる。炭素系導電性層の導電性フィラーとしては、カーボンブラックや黒鉛微粒子等が使用できる。具体的には、以下のようにして電極と集電体の間に炭素系導電性層を形成し、電極と集電体とを接合させる。

【0018】例えば、樹脂粉末と導電性フィラー(粉末)とを混合し、得られた混合物を集電体上にほぼ均一となるように振りまき、その上に別途作製したシート状の電極を載せて150℃以上の温度でホットプレスすることにより樹脂をホットメルトさせて電極と集電体を強固に接合できる。

【0019】また、上記樹脂を含むペーストに導電性フィラーを十分に分散させて接着剤とできる。得られた接着剤を集電体の表面に滴下、刷毛塗り、スプレー、バーコータ、ドクターブレード、グラビアコータ、コンマコータ、ダイコータ等によって塗工し、次いでこの表面に別途作製したシート状の電極を圧着し、好ましくは150℃以上の高温下、さらに好ましくは減圧下で加熱することにより、電極と集電体を強固に接合できる。また、接着剤を塗工する場合も加熱方法としてホットプレスしてもよい。

【0020】また、上記樹脂を含むワニスに導電性フィラーを分散させ、ガラスや型離れしやすい紙からなる基材にキャスト製膜して架橋反応が起こるより低い温度、具体的には50～80℃程度で加熱してフィルムを作製する。得られたフィルムは基材から剥離させた後、集電体上に載置し、さらにその上に別途作製したシート状の電極を載置し、150℃以上の温度でホットプレスすることにより樹脂をホットメルトさせて電極と集電体を強固に接合できる。

【0021】上に挙げた方法において、ホットプレスする場合は、150℃以上、特に150～250℃、さらには200～250℃であることが好ましい。通常、熱

硬化型のポリカルボジイミド樹脂は150℃以上で硬化する。また、熱分解温度は300℃以上であるため、ホットプレスする温度はポリカルボジイミド樹脂のみについて考えれば150～300℃の範囲内で高い方が好ましいが、シート状の電極に含まれる結合材の耐熱温度を考慮する必要がある。例えば前記結合材としてPTFEを使用する場合は、250℃を超えるとPTFEの繊維の切断が起こるので、250℃以下でホットプレスすることが必要である。

【0022】また、ホットプレスする場合のプレス圧は3～50MPaが好ましい。プレス圧を上げるほど電極と集電体との密着性は向上するが、例えば集電体の一部に電極を接合させずにその部分を集電タブとして用いる場合は、過剰の圧力がかかることにより集電タブの部分と電極が接合されている集電体の部分とで、集電体の伸びに差が生じる。そのため、これらの部分の境界部において湾曲や切断等の不具合が起こるので好ましくない。

【0023】また、上記において用いたシート状の電極は、炭素質粉末と結合材とを含む混合物をシート状に成形して得られる炭素質電極である。結合材としては、含フッ素樹脂が有機溶媒に対する耐性が高く好ましいが、特にPTFEが好ましい。シート状電極作製時においてPTFEを繊維化させることにより、電極の抵抗を高くせずに高強度のシート状電極を得ることができる。PTFEは、炭素質粉末とPTFEとの混合物を混練することにより繊維化するが、ペースト押出し成形やスクリーン押出し成形のような押出し成形により繊維化させることもできる。

【0024】本発明では、バインダ成分であるポリカルボジイミド樹脂は炭素系導電性層全質量中に10～70%、特に20～50%含まれることが好ましい。ポリカルボジイミド樹脂が炭素系導電性層中に10%以上含まれることによって実用的な高い接合強度が得られる。一方、あまり多く含まれると接着層の電気抵抗が大きくなるので、70%以下とするのが好ましい。

【0025】なかでもR<sup>1</sup>R<sup>2</sup>R<sup>3</sup>R<sup>4</sup>N<sup>+</sup>、R<sup>1</sup>R<sup>2</sup>R<sup>3</sup>R<sup>4</sup>P<sup>+</sup>(R<sup>1</sup>、R<sup>2</sup>、R<sup>3</sup>及びR<sup>4</sup>はそれぞれ独立にアルキル基。)等の第4級オニウムカチオンと、BF<sub>4</sub><sup>-</sup>、PF<sub>6</sub><sup>-</sup>、ClO<sub>4</sub><sup>-</sup>、CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>等のアニオンとからなる第4級オニウム塩を有機溶媒に溶解させた有機電解液を使用するのが好ましい。

【0026】上記有機溶媒としては、プロピレンカーボネート、ブチレンカーボネート、ジエチルカーボネート等のカーボネート類、γ-ブチロラクトン等のラクトン

類、スルホラン、アセトニトリル又はこれらの混合溶媒が好ましく使用できる。

【0027】本発明の電気二重層キャパシタの炭素質電極の材料としては、電気化学的に不活性な高比表面積の材料であれば使用できるが、高比表面積を有する活性炭粉末を主体として炭素質電極を形成するのが好ましい。活性炭粉末以外にも、カーボンブラック、ポリアセン等の大比表面積の材料も好ましく使用できる。本発明では炭素質電極を使用するが、その他に電気二重層キャパシタの電極材料として金属微粒子、導電性金属酸化物微粒子等の高比表面積の材料も使用できることが知られている。

【0028】また、炭素質電極を正極と負極の両方に用いて電気二重層キャパシタとする以外に、正極又は負極の一方のみを上記炭素質電極とし、残りの一方を充放電可能な非炭素質粉末電極材料、すなわち二次電池用活物質材料を主とする非炭素質電極とすることもできる。

【0029】上記の炭素質電極を電気的に接続するための集電体は、導電性に優れ、かつ電気化学的に耐久性のある材料であればよく、アルミニウム、チタン、タンタルなどのバルブ金属、ステンレス鋼、金、白金などの貴金属、黒鉛、グラッシーカーボン、カーボンブラックを含む導電性ゴム等の炭素系材料が好ましい。

【0030】

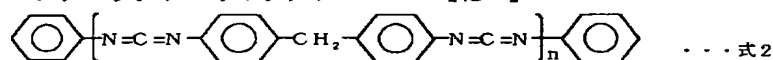
【実施例】以下、本発明を実施例(例1～4)及び比較例(例5)によってさらに説明するが、本発明はこれらに限定されない。

【0031】[例1]フェノール樹脂を原料とし、水蒸気賦活法で得られた活性炭粉末(平均粒径10μm、比表面積2000m<sup>2</sup>/g)と、PTFEとカーボンブラックとを質量比で8:1:1となるように混合し、エタノールを加えて混練した。次いで混練物をシート状に成形し、さらに厚さ0.3mmにロール圧延後、40mm角の電極シートを切り取った。

【0032】次に、230gのキシレン中に63gの4,4'-ジフェニルメタンジイソシアネートと6.7gのイソシアネ酸フェニルと0.14gの3-メチルー1-フェニルー2-ホスホレン 1-オキソドを混合し、110℃で12時間反応させ、質量比で20%樹脂濃度のポリカルボジイミド樹脂の溶液を得た。溶質の樹脂は、式2で表される構造を有していた。ただし、nは正の整数である。

【0033】

【化2】



・・・式2

【0034】この溶液300gに、120gの黒鉛微粒子と120gのカーボンブラックと460gのキシレンを混合し、ボールミルで12時間混合して固形分が全質量の30%(固形分の各成分の含有割合は、ポリカルボ

ジイミド樹脂:黒鉛微粒子:カーボンブラック=20:40:40)の導電性接着剤を得た。

【0035】次にエッチング処理を施した厚さ0.1mmのアルミニウム箔からなる集電体の表面に、上記導電

性接着剤を塗工し、上記電極シートをその塗工面に圧着し、250℃において減圧下で3時間加熱して乾燥処理し、電極中の水分を除去した電極体を得た。

【0036】次にこの電極体をアルゴンガスを充填したグローブボックスに移し、有機電解液として1mol/Lのテトラエチルアンモニウムテトラフルオロボレートを含むプロピレンカーボネート溶液を電極に充分に含浸させた。一対の電極体をポリプロピレン繊維の不織布からなるセパレータ紙を挟んで電極シートが接合されている面どうしを対向させ、電気二重層キャパシタを組み立てた。

【0037】得られた電気二重層キャパシタの初期の放電容量及び内部抵抗を測定した後、40℃の恒温槽中で0～2.8Vの間で1Aの定電流による充放電を3000サイクル繰り返し、3000サイクル後の放電容量及び内部抵抗を測定し、初期と充放電サイクル後の性能変化を観察することにより、電気二重層キャパシタの長期的な作動信頼性を加速的に評価した。結果を表1に示す。

【0038】【例2】例1で得られたポリカルボジミド樹脂の溶液300gに500gのヘキサンを添加して固体を析出させ、析出した固体をろ過して150℃で2時間真空乾燥してポリカルボジミド樹脂を得た。20gのポリカルボジミド樹脂と40gの黒鉛微粒子と40gのカーボンブラックとを混合し、ボールミルで12時間混合してポリカルボジミド：黒鉛微粒子：カーボンブラック＝20：40：40の混合粉末を得た。

【0039】エッチング処理を施した厚さ0.1mmのアルミニウム箔からなる集電体の表面に、上記混合粉末を塗工量が150g/m<sup>2</sup>程度となるように振りまいて、その上に例1と同じ電極シートを載置し、150℃に加熱したホットプレスにて4.8MPaの圧力を10分間かけ、電極体を得た。この電極体を使用した以外は例1と同様に電気二重層キャパシタを組み立て、例1と同様に評価した。結果を表1に示す。

【0040】【例3】ペースト状のポリカルボジミド樹脂として日清紡社製のカルボジライトAF-F4（商品名）を使用し、導電性フィラーとして黒鉛とカーボンブラックを用い、ポリカルボジミド：黒鉛微粒子：カーボンブラック＝20：40：40の導電性ペーストを得た。この導電性ペーストを、エッチング処理を施した厚さ0.1mmのアルミニウム箔からなる集電体の表面に、バーコートを用いて15g/m<sup>2</sup>の塗工量となるように塗工し、その上に例1と同じ電極シートを載置して

160℃で20分間加熱して電極体を得た。例1と同様に電気二重層キャパシタを組み立て、例1と同様に評価した。結果を表1に示す。

【0041】【例4】テトラヒドロフラン2000g中に125gの4,4'-ジフェニルメタンジイソシアネートと0.3gの3-メチル-1-フェニル-2-ホスホレン-1-オキシドとを投入し、60℃で25時間還流して反応させ、ポリカルボジミド溶液を得た。この溶液に黒鉛微粒子50gとカーボンブラック50gとを混合分散させた。得られたスラリーを用いてガラス上にキャスト製膜し、60℃で5時間乾燥して溶媒を除去し厚さ20μmのフィルムを得た。

【0042】このフィルムをエッチング処理を施した厚さ0.1mmのアルミニウム箔からなる集電体の表面に載置し、その上に例1と同じ電極シートを載置して150℃に加熱したホットプレスにて4.8MPaの圧力を10分間かけ、電極体を得た。この電極体を使用した以外は例1と同様に電気二重層キャパシタを組み立て、例1と同様に評価した。結果を表1に示す。

【0043】【例5】ポリカルボジミド樹脂の溶液のかわりに、N-メチル-2-ピロリドンに固形分濃度20%でポリフッ化ビニリデン樹脂が溶解した溶液300gを使用した以外は例2と同様にして黒鉛微粒子とカーボンブラックとを混合した導電性接着剤を得た。ポリフッ化ビニリデン樹脂は耐熱温度が160℃以下であるため、減圧下で250℃で加熱するかわりに真空中で120℃で加熱した。それ以外は例1と同様にして電極体を得て、例1と同様にして電気二重層キャパシタを組み立て、例1と同様に評価した。結果を表1に示す。

【0044】

【表1】

	初期特性		サイクル試験後	
	容量/F	内部抵抗/Ω	容量/F	内部抵抗/Ω
例1	16.8	0.48	15.9	0.56
例2	16.3	0.46	15.5	0.51
例3	15.6	0.53	14.4	0.63
例4	15.8	0.55	15.3	0.59
例5	15.1	0.62	8.8	1.08

【0045】

【発明の効果】本発明の電気二重層キャパシタは、高温の加速的劣化を起こす試験条件下において充放電サイクルを繰り返した時の容量劣化と内部抵抗の上昇が顕著に小さく、長期間使用時の作動信頼性に優れている。

フロントページの続き

(72)発明者 吉田 直樹  
神奈川県横浜市神奈川区羽沢町1150番地  
旭硝子株式会社内

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(54) [TITLE OF THE INVENTION] ELECTRIC DOUBLE-LAYER CAPACITOR, ELECTRODE BODY THEREOF, AND METHOD OF PRODUCING THE SAME

(57) [ABSTRACT]

[OBJECT] To provide an electric double-layer capacitor which has excellent performance resistant to a deterioration caused by charge and discharge cycles and ensures a highly reliable long-term operation.

[SOLVING MEANS] In an electric double-layer capacitor having an organic electrolytic solution, an electrode body in which a carbonaceous electrode molded into a sheet form and having activated carbon as its main component is bound with a current collector through a carbonic conductive layer containing a polycarbodiimide resin as a binder component is used.

[SCOPE OF CLAIMS FOR PATENT]

[Claim 1]

An electric double-layer capacitor comprising: a sheet-shaped electrode containing a carbonaceous powder and a binder; and an organic electrolytic solution forming an electric double-layer on the surface of the electrode, wherein said electrode is bound with a current collector through a carbonic conductive layer containing a polycarbodiimide resin as a binder component.

[Claim 2]

An electric double-layer capacitor according to Claim 1, wherein the polycarbodiimide resin is contained in an amount of 10 to 70% in the total weight of the carbonic conductive layer.

[Claim 3]

An electric double-layer capacitor according to Claim 1 or 2, wherein the organic electrolytic solution is an electrolytic solution prepared by dissolving a quaternary onium salt in an organic solvent.

[Claim 4]

An electric double-layer capacitor electrode comprising a sheet-shaped electrode containing a carbonaceous powder and a binder, the electrode being bound with a current collector through a carbonic conductive layer containing a polycarbodiimide resin as a binder component.

[Claim 5]

A method of producing an electric double-layer capacitor electrode, the method comprising: molding a mixture of a carbonaceous powder and a binder into a sheet form to form a carbonaceous electrode; binding the carbonaceous electrode with a current collector through a carbonic conductive layer containing a polycarbodiimide resin as a binder component; and heating the resulting product at 150°C or more.

[Claim 6]

A method of producing an electric double-layer capacitor electrode according to Claim 5, wherein said conductive layer is formed by making a mixed powder, a slurry or a film containing a polycarbodiimide resin and a conductive filler to be placed on or applied to the current collector, and said carbonaceous electrode is placed on the conductive layer, followed by hot-pressing.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[TECHNICAL FIELD PERTINENT TO THE INVENTION]



The present invention relates to an electric double-layer capacitor and, particularly, to an electric double-layer capacitor superior in operational reliability and also to an electrode body used for the capacitor.

[0002]

[CONVENTIONAL ART]

Electric double-layer capacitors works based on the principle that charges are accumulated in an electric double-layer formed in an electrolytic solution on the surface of a carbonaceous electrode. In order to improve the capacitance density of the electric double-layer capacitor, carbon materials, such as activated carbon, carbon black and polyacene, which have a high specific surface area are used. Also, there is the case where an electrode comprising metal or conductive metal oxide microparticles is used. In order to charge and discharge the carbonaceous electrode having a high specific surface area efficiently, the carbonaceous electrode is bound with a layer or a foil called a current collector and made of, for example, metal or graphite which has electronic conductivity and small resistance. As the current collector, a valve metal such as aluminum or stainless steel such as SUS 304 and SUS 316L having electrochemically high corrosion resistance is usually used.

[0003]

The electric double-layer capacitor includes types using an organic electrolytic solution or an aqueous electrolytic solution as the above electrolytic solution. Among these types, electric double-layer capacitors using an organic electrolytic solution attract attention because it is operated at high voltages and enables energy density to be increased in the charged

state. In the case of using an organic electrolytic solution, the presence of moisture in the electric double-layer capacitor allows the moisture to be electrolyzed, bringing about a deterioration in the performance of the capacitor. It is therefore necessary to carry out dehydration of the above carbonaceous electrode to a high degree. For this, drying treatment is usually carried under reduced pressure and heating.

[0004]

As the carbonaceous electrode, activated carbon is mainly used. Since activated carbon has generally a powder form, it is molded into a sheet form in advance by using a binder containing a fluororesin such as polytetrafluoroethylene (hereinafter referred to as PTFE). The molded carbon is electrically connected with a current collector and used as an electrode body. In this case, there is a type in which the electrode is made to be in closed contact with the current collector and also the both are bound with each other via a conductive adhesive layer to reduce electrically contact resistance. However, the fluororesins are of such a nature that it is difficult to stick these resins and it is therefore possible to obtain large binding strength.

[0005]

The conductive adhesive layers require electrochemical corrosion resistance and carbon materials such as carbon black and graphite are preferably used as the filler that imparts electronic conductivity to these conductive adhesive layers. Moreover, various binder components are used in the conductive adhesive layer to secure binding strength. As the binder component used for this purpose, celluloses and resins such as polyvinyl

alcohols (e.g., JP-A 59-3915 and JP-A 62-200715), and inorganic binder components such as water glass (JP-A 2-82608) are known.

[0006]

However, when a conductive adhesive containing the above resin as a binder component is used, unsatisfactory resistance to the organic electrolytic solution affords a possibility of the carbonaceous electrode being peeled from the current collector. Also, as to the heat resistance of even a binder having high heat resistance, the temperature at which it can stand is around 150°C and therefore, this binder cannot stand to dry treatment carried out at high temperatures. If the electric double-layer capacitor is used for a long period of time, there is, for example, the problem that the presence of residual moisture in the electric double-layer capacitor allows the moisture to be electrolyzed, bringing about a deterioration in the performance of the capacitor. Also, in the case of inorganic binders such as water glass, these binders have high heat resistance; however each has inferior adhesive strength to the metal current collector, giving rise to the problem that the performance of the electric double-layer capacitor is deteriorated by the elution of alkali components and residual moisture.

[0007]

#### [PROBLEM TO BE SOLVED BY THE INVENTION]

It is an object of the present invention to solve the above prior art problems, and specifically, to provide an electric double-layer capacitor which can decrease moisture to a level as low as possible in a capacitor, particularly, in a carbonaceous electrode, is provided with an electrode and a current collector which are firmly bound electrically with each other, and is

resistant to deterioration in performance.

[0008]

[MEANS FOR SOLVING THE PROBLEM]

According to the present invention, there is provided an electric double-layer capacitor comprising: a sheet-shaped electrode containing a carbonaceous powder and a binder; and an organic electrolytic solution forming an electric double-layer on the surface of the electrode, wherein the electrode is bound with a current collector through a carbonic conductive layer containing a polycarbodiimide resin as a binder component, and there is also provided an electrode body used for the capacitor.

[0009]

Also, the present invention provide a method of producing an electric double-layer capacitor electrode, the method comprising: molding a mixture of a carbonaceous powder and a binder into a sheet form to form a carbonaceous electrode; binding the carbonaceous electrode with a current collector through a carbonic conductive layer containing a polycarbodiimide resin as a binder component; and heating the resulting product at 150°C or more.

[0010]

[EMBODIMENTS OF THE INVENTION]

In this specification, a material obtained by integrating a carbonaceous electrode containing a carbonaceous powder and a binder with a current collector is called an electrode body. This electrode body is called a positive electrode body when used on the positive electrode side and a negative electrode body when used on the negative electrode side.

[0011]

In the electric double-layer capacitor of the present invention, the binder contained in the carbonaceous electrode is a polycarbodiimide resin. The heat resistant temperature of this resin is generally in a range from 200 to 400°C and this resin has high heat resistance. The polycarbodiimide resin is a generic name of resins having a carbodiimide group skeleton ( $\text{-N=C=N-}$ ) at the primary chain and is superior in chemical resistance, mechanical characteristics, dimensional stability and electrical characteristics.

[0012]

The polycarbodiimide resin is melted and enters into a crosslinking reaction under heating, whereby it is cured. Moreover, if a crosslinking agent having two or more reactive groups in its molecule is mixed in the polycarbodiimide resin and the mixture is heated, the polycarbodiimide resin is cured by heating in an efficient manner. The internal crosslinking reaction of the polycarbodiimide resin is, for example, one represented by the formula 1.

[0013]

Formula 1

[0014]

As the polycarbodiimide resin used in the present invention, specifically, polycarbodiimide resins represented by, for example,  $\text{R}^1\text{-(N=C=N-R}^2\text{-N=C=N-)}_m\text{-R}^3$  are preferably used. In the formula,  $\text{R}^1$  and  $\text{R}^3$  respectively represent a monovalent organic group,  $\text{R}^2$  represents a

divalent organic group and  $m$  denotes a positive integer. As mentioned above, the polycarbodiimide resin is preferably obtained by reacting raw materials including  $\text{OCN-R}^2\text{-NCO}$ ,  $\text{R}^1\text{-NCO}$  and  $\text{R}^3\text{-NCO}$ .

[0015]

Examples of commercially available products of the polycarbodiimide resin include powder resins, solutions (varnish) obtained by dissolving resins in a solvent, paste-like resins containing no solvent and resins molded into a film form. Among these forms, the paste and varnish are preferable because a coating solution is easily produced. Examples of a commercially available varnish of the polycarbodiimide resin include "CARBODILITE" manufactured by Nisshinbo Industries, Inc.

[0016]

In the electric double-layer capacitor electrode body according to the present invention, the polycarbodiimide resin which is a binder component of the carbonic conductive layer has high heat resistance and therefore the electrode can be dried to remove moisture contained therein completely by heat treatment at high temperatures or heat treatment under reduced pressure. Also, the polycarbodiimide resin is resistant to an organic electrolytic solution and also, makes it possible to remarkably heighten the adhesive strength between the electrode sheet and the current collector even if a fluororesin is contained as the binder of the electrode sheet. For this, even if a charge and discharge cycle is repeated at a large current density and even if voltage is applied for a long period of time, the working performance of the electric double-layer capacitor is stable and an increase in the internal resistance of the electrode can be decreased.

[0017]

The resin used for the binder component may also be used as a resin powder, as it is as a paste, as a slurry prepared by dispersing a powder of the resin, varnish containing the resin or the resin having a paste form or as a film prepared by molding it. As the conductive filler of the carbonic conductive layer, carbon black, graphite microparticles and the like may be used. Specifically, the carbonic conductive layer is formed between the electrode and the current collector and the electrode is bound with the current collector.

[0018]

For example, the resin powder and the conductive filler (powder) are mixed with each other and the resulting mixture is scattered almost uniformly on the current collector. A sheet electrode produced separately is placed on the scattered mixture, which is then subjected to hot-pressing carried out at 150°C or more, whereby the resin can be hot-melted to bind the electrode firmly with the current collector.

[0019]

Also, a conductive filler is sufficiently dispersed in a paste containing the above resin to make an adhesive. The resulting adhesive is dripped on and applied to the surface of the current collector by brush coating, or by using a spray, bar coater, doctor blade, gravure coater, comma coater, die coater or the like. Then, a sheet electrode produced separately is stuck under pressure to the surface of the adhesive, which is then heated at a temperature of, preferably 150°C or more and more preferably under reduced pressure, whereby the electrode can be bound firmly with the

current collector. Also, in the case of applying an adhesive, a heating method using a hot press may be used.

[0020]

Also, a conductive filler is dispersed in varnish containing the above resin and the resulting varnish is applied by cast coating to a base material made of glass or releasable paper. Then, the coating layer is heated at a temperature lower than the temperature at which a crosslinking reaction takes place, specifically at 50 to 80°C, to produce a film. The resulting film is peeled from the base material and is then placed on the current collector. Furthermore, a sheet electrode produced separately is placed on the film and is then hot-pressed at a temperature of 150°C or more to thereby hot-melt the resin, thereby binding the electrode with the current collector firmly.

[0021]

In the method mentioned above, the temperature in the case of carrying out hot-pressing is preferably 150°C or more, more preferably 150 to 250°C and still more preferably 200 to 250°C. Generally, a heatcurable type polycarbodiimide resin is cured at 150°C or more. Also, because the heat decomposition temperature of the resin is 300°C or more, the hot-pressing temperature is preferably higher in a range from 150 to 300°C taking only the polycarbodiimide resin into account. However, the heat resistant temperature of the binder contained in the sheet electrode must be taken into account. In the case of using, for example, PTFE as the binder, PTFE fibers are cut at temperatures exceeding 250°C and it is therefore necessary to carry out hot-pressing at a temperature of 250°C or less.



[0022]

Also, the pressing pressure in the case of carrying out hot-pressing is preferably 3 to 50 MPa. The adhesion between the electrode and the current collector is more improved as the pressing pressure is increased. However, for example, in the case where a part of the current collector is not bound with the electrode but is used as a current collector tab, excess pressure causes a difference in the extension of the current collector between the part of the current collector tab and the part of the current collector with which part the electrode is bound. This causes disorders such as curvature and breaking at the boundary between these parts and excess pressure is undesirable.

[0023]

Also, the sheet electrode used above is a carbonaceous electrode obtained by molding a mixture containing a carbonaceous powder and a binder into a sheet form. As the binder, fluororesins are preferably used because it is highly resistant to an organic solvent. Among these fluororesins, PTFEs are particularly preferable. This PTFE is made into fibrous material in the production of the sheet electrode, which makes it possible to obtain a sheet electrode having high strength without increasing the resistance of the electrode. The PTFE is made into fibrous material by kneading a mixture of the carbonaceous powder and PTFE. Extrusion molding such as paste extrusion molding or screw extrusion molding may be used to make the fibrous material.

[0024]

In the present invention, the polycarbodiimide resin that is the binder

component is contained in an amount of, preferably, 10 to 70% and particularly preferably 20 to 50% based on the total weight of the carbonic conductive layer. When the polycarbodiimide resin is contained in the carbonic conductive layer in an amount of 10% or more, practically high binding strength is obtained. If this resin is contained too much, the electric resistance of the adhesive layer is increased and the amount of this resin is therefore preferably 70% or less.

[0025]

It is particularly preferable to use an organic electrolytic solution obtained by dissolving a quaternary onium salt comprising a quaternary onium cation represented by, for example,  $R^1R^2R^3R^4N^+$  or  $R^1R^2R^3R^4P^+$  ( $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  respectively represent an alkyl group) and an anion such as  $BF_4^-$ ,  $PF_6^-$ ,  $ClO_4^-$  or  $CF_3SO_3^-$ .

[0026]

As the above organic solvent, carbonates such as propylene carbonate, butylene carbonate and diethyl carbonate, lactones such as  $\gamma$ -butyrolactone, sulfolane and acetonitrile or mixed solvents of these compounds are preferably used.

[0027]

As the carbonaceous electrode material of the electric double-layer capacitor of the present invention, any material may be used insofar as it is an electrochemically inert material having a high specific surface area. It is however desirable to form the carbonaceous electrode by primarily using an activated carbon powder having a high specific surface area. Besides the activated carbon powder, materials having a large specific surface area such

as carbon black and polyacene are also used. Although the carbonaceous electrode is used in the present invention, it is known that, other than the above, materials having a high specific surface area such as metal microparticles and conductive metal oxide microparticles may also be used as the electrode material of the electric double-layer capacitor.

[0028]

Also, other than the embodiment in which the carbonaceous electrode is used as each of the positive and negative electrodes to make the electric double-layer capacitor, the carbonaceous electrode is used as only one of the positive and negative electrodes and a non-carbonaceous powder electrode material, specifically, secondary battery activated material, which can be charged and discharged may be primarily used as the reminder electrode.

[0029]

Any material may be used as the above current collector that is electrically connected with the carbonaceous electrode insofar as it is a material having high conductivity and electrochemical durability. As the current collector, valve metals such as aluminum, titanium and tantalum, stainless steel, precious metals such as gold and platinum and carbon type materials such as graphite, glassy carbon and conductive rubber containing carbon black are preferable.

[0030]

[EXAMPLES]

The present invention will be further described by way of examples (Examples 1 to 4) and a comparative example (Comparative Example 5), which, however, are not intended to be limiting of the invention.

[0031]

[Example 1]

An activated carbon powder (average particle diameter: 10  $\mu\text{m}$ , specific surface area: 2000  $\text{m}^2/\text{g}$ ) obtained using a phenol resin as a raw material by a steam activation method and PTFE and carbon black were mixed in a ratio by weight of 8 : 1 : 1 and ethanol was added to the mixture, which was then kneaded. Then, the kneaded product was molded into a sheet form, which was further rolled to a thickness of 0.3 mm to cut a 40-mm-square electrode sheet out of the rolled sheet.

[0032]

Next, 63 g of 4,4'-diphenylmethanediisocyanate, 6.7 g of phenylisocyanate and 0.14 g of 3-methyl-1-phenyl-2-phosphorene 1-oxide were mixed in 230 g of xylene and the mixture was reacted at 110°C for 12 hours, to obtain a solution (resin concentration: 20% by weight) of a polycarbodiimide resin. The resin which was a solute had the structure shown by the formula 2, wherein n is a positive integer.

[0033]

Formula 2

[0034]

120 g of graphite microparticles, 120 g of carbon black and 460 g of xylene were mixed in 300 g of the above resulting solution and these components were mixed in a ball mill for 12 hours to obtain a conductive adhesive having a solid content of 30% based on the total weight (the proportion of

each component of the solid content: polycarbodiimide resin : graphite microparticles : carbon black = 20 : 40 : 40).

[0035]

Then, the above conductive adhesive was applied to the surface of a 0.1-mm-thick aluminum foil which had been subjected to etching treatment and the above electrode sheet was stuck to the coated surface under pressure. The resulting electrode body was heated at 250°C under reduced pressure for 3 hours to carry out drying treatment, to thereby obtain an electrode body from which moisture in the electrode was removed.

[0036]

Next, this electrode body was transferred to a gloved box filled with argon gas and the electrode was fully impregnated with an organic electrolytic solution comprising a propylene carbonate solution containing 1 mol/L of tetraethylammonium tetrafluoroborate. A pair of electrodes which were each the above electrode were disposed such that the surfaces of the both which surfaces were not respectively bound with the electrode sheet were facing each other through a separator paper made of polypropylene fiber nonwoven fabric, to thereby fabricate an electric double-layer capacitor.

[0037]

The initial discharge capacity and internal resistance of the obtained electric double-layer capacitor were measured. Then, a charge and discharge operation performed under a constant current of 1 A in a voltage range from 0 to 2.8 V was repeated for a total of 3000 cycles in a constant temperature bath at 40°C to measure the discharge capacity and internal resistance after 3000 cycles and to observe a change in characteristics of the

capacitor after 3000 cycles from those in the initial stage, thereby evaluating the long-term operational reliability of the electric double-layer capacitor in an accelerated test. The results are shown in Table 1.

[0038]

[Example 2]

500 g of hexane was added to 300 g of the polycarbodiimide resin solution obtained in Example 1 to precipitate a solid, and the precipitated solid was collected by filtration and dried at 150°C under vacuum for 2 hours to obtain a polycarbodiimide resin. 20 g of the polycarbodiimide resin, 40 g of graphite microparticles and 40 g of carbon black were formulated and mixed by a ball mill for 12 hours to obtain a mixture powder (polycarbodiimide : graphite microparticles : carbon black = 20 : 40 : 40).

[0039]

The above mixture powder was scattered on the surface of a current collector made of a 0.1-mm-thick aluminum foil which had been subjected to etching treatment in an coating amount of about 150 g/m<sup>2</sup>. The same electrode sheet that was used in Example 1 was placed on the mixture powder to apply a pressure of 4.8 MPa to the surface of the sheet by a hot press heated to 150°C for 10 minutes, and an electrode body was thus obtained. An electric double-layer capacitor was fabricated in the same manner as in Example 1 except that this electrode body was used and evaluated in the same manner as in Example 1. The results are shown in Table 1.

[0040]

[Example 3]

CARBODILITE AF-F4 (trade name, made by Nisshinbo Industries, Inc.) was used as a paste-like polycarbodiimide resin and graphite and carbon black were used as conductive fillers to obtain a conductive paste having the following composition: CARBODILITE : graphite microparticles : carbon black = 20 : 40 : 40. Then, this conductive paste was applied to the surface of a 0.1-mm-thick aluminum foil which had been subjected to etching treatment, by using a bar coater in a coating amount of 15 g/m<sup>2</sup> and the same electrode sheet that was used in Example 1 was placed on the coating layer, followed by heating at 160°C for 20 minutes to obtain an electrode body. An electric double-layer capacitor was fabricated and evaluated in the same manner as in Example 1. The results are shown in Table 1.

[0041]

[Example 4]

125 g of 4,4'-diphenylmethanediisocyanate and 0.3 g of 3-methyl-1-phenyl-2-phosphorene 1-oxide were poured into 2000 g of tetrahydrofuran and the mixture was refluxed under heating at 60°C for 25 hours to react, thereby obtaining a polycarbodiimide solution. 50 g of graphite microparticles and 50 g of carbon black were mixed and dispersed in this solution. Using the obtained slurry, it was formed as a film by casting and then dried at 60°C for 5 hours to remove solvents, thereby obtaining a 20-μm-thick film.

[0042]

This film was placed on the surface of a current collector made of a 0.1-mm-thick aluminum foil which had been subjected to etching treatment. The same electrode sheet that was used in Example 1 was placed on the film

to apply a pressure of 4.8 MPa to the surface of the sheet by a hot press heated to 150°C for 10 minutes, and an electrode body was thus obtained. An electric double-layer capacitor was fabricated in the same manner as in Example 1 except that this electrode body was used and evaluated in the same manner as in Example 1. The results are shown in Table 1.

[0043]

[Example 5]

A conductive adhesive in which graphite microparticles and carbon black were mixed was obtained in the same manner as in Example 2 except that 300 g of a solution (solid content: 20%) obtained by dissolving a polyvinylidene fluoride resin in N-methyl-2-pyrrolidone was used in place of the polycarbodiimide resin solution. Because the polyvinylidene fluoride resin had a heat resistant temperature of 160°C or less, it was heated at 120°C under vacuum instead of heating it at 250°C under reduced pressure. An electrode body was obtained in the same manner as in Example 1 except for the above process. An electric double-layer capacitor was fabricated and evaluated in the same manner as in Example 1. The results are shown in Table 1.

[0044]

[Table 1]

	Initial characteristics		After cycle test	
	Capacitance/F	Internal resistance/ $\Omega$	Capacitance/F	Internal resistance/ $\Omega$
Ex. 1	16.8	0.48	15.9	0.56
Ex. 2	16.3	0.46	15.5	0.51



Ex. 3	15.6	0.53	14.4	0.63
Ex. 4	15.8	0.55	15.3	0.59
Ex. 5	15.1	0.62	8.8	1.08

[0045]

#### [EFFECT OF THE INVENTION]

The electric double-layer capacitor of the present invention is significantly resistant to a deterioration in capacitance and to a rise of internal resistance when a charge and discharge operation is repeated under test conditions which accelerate a deterioration at a high temperature and is also superior in operational reliability when it is used for a long time.

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